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Review

Photoluminescence properties of Tb^{3+}-doped sodalite under VUV–UV light excitation

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A B S T R A C T

Natural sodalite ($Na_8Al_6Si_6O_{24}Cl_2$) from Xinjiang, China, was activated with TbF_3 by a high-temperature melting method and green luminescence phosphors were synthesized. The results of X-ray diffraction (XRD) test showed that the main crystal phase of the sample heat-treated at 1100 °C was sodalite, but the NaCl component in the sample was partially lost by the heat treatment and the minor content of nepheline (hexagonal) structure (syn. $NaAlSiO_4$) was created. The vacuum ultra-violet (VUV) light excitation spectrum, obtained by monitoring the green luminescence at 541 nm, consisted of excitation bands with peaks at 174 and 222 nm. These excitation bands were assigned to the absorption band by the host crystal and the spin-allowed $4f^8$–$4f^7 5d$ transitions within Tb^{3+}, respectively. The emission spectra under VUV–UV light excitation consisted of a series of narrow bands corresponding to the $^5D_3 \rightarrow {}^7F_J$ ($J=6$, 5, 4, 3 and 2) and $^5D_4 \rightarrow {}^7F_J$ ($J=6$, 5, 4 and 3) transitions within Tb^{3+}. The predominant band at 541 nm corresponds to the $^5D_4 \rightarrow {}^7F_5$ transition. The lifetime of luminescence corresponding to the $^5D_3 \rightarrow {}^7F_J$ ($J=6$, 5 and 4) transitions was 1.2 ms, while the lifetimes of luminescence corresponding to the $^5D_4 \rightarrow {}^7F_J$ ($J=6$ and 5) transitions were 2.5 and 2.8 ms, respectively. The CIE (Commission Internationale de l'Éclairage) chromaticity coordinate of luminescence from the sample was (0.287, 0.301) and the correlated chromaticity temperature was 8796 K.

Contents

1. Introduction

As the host materials of phosphors, natural minerals have advantages such as abundant resources, low production cost and simple technology; thus natural minerals are quite promising in terms of application. At present, the research and development of

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mineral functional materials are extremely valued in various countries [1,2]. Based on nontoxicity, chemical stability and heat resistance, silicate minerals are taken as a type of clean light source and most are used as the substrate of luminescent materials [3].

Natural sodalite with the ideal chemical formula $Na_8Al_6Si_6O_{24}Cl_2$ or $3(Na_2O \cdot Al_2O_3 \cdot 2SiO_2) \cdot 2NaCl$ is a typical silicate mineral. Compared with other minerals, sodalite is a research focus in the field of the luminescence due to its distinctive physical and chemical properties and advantages. Aierken et al. [4] reported on the photoluminescence (PL) properties of the S_2^- center in natural sodalite ($Na_8Al_6Si_6O_{24}Cl_2$), and conducted a comparative study of sodalite samples from Greenland, Canada, Xinjiang and other areas. Reliable curves of the emission and excitation spectra of the S_2^- center in sodalite at temperatures of 300 and 10 K were provided. Muyasier et al. [5] reported the PL properties of green and red luminescence from natural and heat-treated sodalite ($Na_8Al_6Si_6O_{24}Cl_2$) from Xinjiang. Gaft et al. [6] observed the laser-induced time-resolved luminescence spectra of silicon beryllium aluminum sodalite ($Na_8Al_6Si_6O_{24}Cl_2$), natural tugtupite ($Na_8Al_2Be_2Si_8O_{24}Cl_2$) and hackmanite ($Na_8Al_6Si_6O_{24}(Cl_2,S)$). Alitunguli et al. [7] reported on the PL properties of the Cu-doped sodalite samples ($Na_8Al_6Si_6O_{24}Cl_2$:Cu^+), as well as phosphor emitting clear blue luminescence under short-wave UV light (Hg 253.7 nm). Liao et al. [8] reported that hackmanite ($Na_8Al_6Si_6O_{24}(Cl_2,S)$) was a good photochromic material, and that its discoloration effect was caused by the color center. Cooper et al. [9] synthesized sodalite molecular sieve materials in ionic liquids for the first time, and created a new thermal synthesis method for ionic liquids.

The luminescence due to various rare-earth (RE) ions in minerals has been widely applied to electric goods. Natural minerals doped with RE elements are usually processed under high temperature solid-state reaction to produce various new functional materials. Phosphors activated with Tb^{3+} exhibit characteristic green luminescence which may be used as the green part in three-band fluorescent materials. Aierken et al. [10] studied the PL properties of Na_2SO_4:RE^{3+} (Ce^{3+}, Sm^{3+}, Tb^{3+}, Dy^{3+} and Tm^{3+}) phosphors prepared of natural thenardite, and reported the emission bands corresponding to the $^5D_3 \rightarrow {}^7F_J$ ($J=6$, 5, 4, 3 and 2) and $^5D_4 \rightarrow {}^7F_J$ ($J=6$, 5, 4, 3, 2, 1 and 0) transitions within Tb^{3+}. Yamashita and Hamada [11] and Yamashita [12]reported the PL properties of the $MgSO_4$:Tb^{3+}, Na^+ powder phosphor as well as PL and thermoluminescence of $MgSO_4$, $CaSO_4$, $SrSO_4$, and $BaSO_4$ powder phosphors activated with Tb^{3+}. Song [13] studied the luminescent properties of Tb^{3+}-doped nano-ZnO, and reported that the best sample preparation parameters were obtained through the relationship between the characteristic green emission intensities and Tb^{3+} concentrations and annealing temperature. He et al. [14] studied the PL properties of $NaSO_4$:Tb^{3+} under UV and VUV light excitation. Blank et al. [15] observed the laser-induced time-resolved luminescence spectra of the Tb^{3+}-doped synthetic zircon and artificial scheelite.

The phosphors activated with RE ions have a rather bright application prospect in plasma display panels (PDP) of large screens, and in non-mercury fluorescent lamps from which mercury pollution is eliminated; thus more and more attention has been placed on the VUV spectral properties of RE ions in different compound systems [16]. In the present work the PL properties of Tb^{3+}-doped sodalite under VUV–UV excitation were studied, to develop luminescent materials which may be used for new and efficient PDP or non-mercury fluorescent lamps.

2. Experimental

Natural sodalite (melting point: 1079 °C, does not include sulfur impurity [5]) from Xinjiang, China, was activated with TbF_3 (melting point: 1172 °C) by a high-temperature melting method. First, broken pieces of natural sodalite were powdered to a uniform consistency using an agate mortar; then TbF_3 (99.99%) with mass fractions of 0.1, 1, 3 and 5 wt% was mixed into the powdered sodalite, and the mixture was ground again. The mixture was placed in a crucible and heated in a muffle at 1100 °C for 20 min in air. After heating, the crucible was placed on an iron plate to cool the sample rapidly to room temperature. After cooling, the samples were broken and ground. The color of the powdered sample was white. Under short-UV light (Hg 253.7 nm) at room temperature, samples exhibited green luminescence and long afterglow was not observed. The strongest green luminescence was emitted from the sample activated with TbF_3 of 1 wt%. In addition, there was no emission under long-UV light (Hg 365.0 nm).

A Shimadzu XRD-7000 X-ray diffractometer (radiation source: $CuK_{\alpha1}$ target, working conditions: 40 kV, 30 mA, $\lambda=0.15406$ nm) was used to determine the X-ray diffraction spectrum of the powder sample. Comparison with the ICCD standard cards 37-0476 for sodalite and 35-0424 for nepheline (hexagonal) structure (syn. $NaAlSiO_4$) was conducted to determine the crystal structure. The microtopography of sample was observed using a Shimadzu-SSX-550 scanning electronic microscope (SEM), operating at 15 kV.

The emission and excitation spectra of the samples under VUV–UV light excitation were measured at Beam-line 4B8 at the Beijing Synchrotron Radiation Facilities (BSRF). The emission and excitation spectra were measured using an ARC 308 fluorescence monochromator, and the detector was a Hamamatsud H8259 photon counting system. The excitation spectra of samples were calibrated with the excitation spectrum of sodium salicylate.

The fluorescence lifetime was determined with an FLS920 fluorescence spectrometer (Edinburgh Instruments); of which the test lifetime was within 50 ps–10 s, spectral response time was 40 ms–200 s, and excitation source was a 100–0.1 Hz LF900 microsecond lamp. The CIE chromaticity coordinates of the sample were measured with EX-1000 exciting spectra and thermal quenching analysis for phosphors system. All samples were tested at room temperature.

3. Results and discussion

3.1. XRD analysis of the samples

Fig. 1 shows the X-ray diffraction patterns of the natural sodalite as well as the 0.1, 1, 3 and 5 wt% TbF_3-doped sodalite samples heat-treated at 1100 °C. The diffraction peak position and

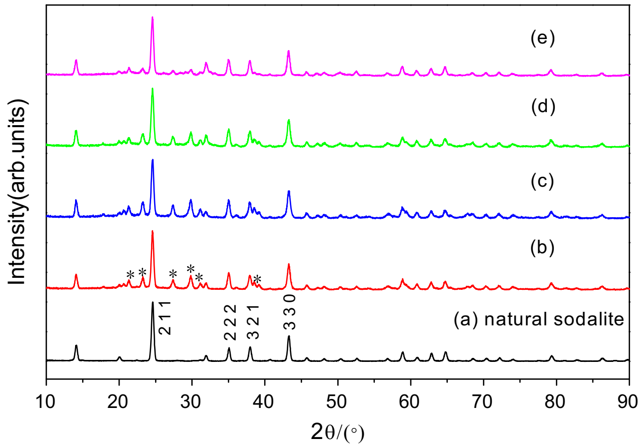

Fig. 1. X-ray diffraction patterns of (a) natural sodalite as well as the (b) 0.1 wt%, (c) 1 wt%, (d) 3 wt% and (e) 5 wt% TbF_3-doped sodalite samples heat-treated at 1100 °C.